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Microwave Sintering and Microwave Dielectric Properties of $(1-x)\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3\text{-}x\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ Ceramics

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Abstract: The $(1-x)\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3\text{-}x\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [(1- x)CLT- x NMT, $x = 0.35\sim 0.60$] ceramics were prepared via microwave sintering. The effects of sintering temperature and composition on the phase formation, microstructure, and microwave dielectric properties were investigated. The results show that the microwave sintering process requires a lower sintering temperature and shorter sintering time of (1- x)CLT- x NMT ceramics than conventional heating methods. All of the (1- x)CLT- x NMT ceramics possess a single perovskite structure. With the increase of x , the dielectric constant (ϵ) shows a downward trend; the quality factor (Qf) drops first and then rises significantly; the resonance frequency temperature coefficient (τ_f) keeps decreasing. With excellent microwave dielectric properties ($\epsilon = 51.3$, $Qf = 13,852$ GHz, $\tau_f = -1.9 \times 10^{-6}/^\circ\text{C}$), the 0.65CLT-0.35NMT ceramic can be applied to the field of mobile communications.

Keywords: (1- x)CLT- x NMT ceramics; microwave sintering; microwave dielectric properties; lattice constant

Citation: Yang, S.; Liang, B.; Liu, C.; Liu, J.; Fang, C.; Ai, Y. Microwave Sintering and Microwave Dielectric Properties of $(1-x)\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3\text{-}x\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ Ceramics. *Materials* **2021**, *14*, 438. <https://doi.org/10.3390/ma14020438>

Received: 28 October 2020

Accepted: 7 January 2021

Published: 17 January 2021

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1. Introduction

With the advent of the 5G era, microwave dielectric ceramics attract more and more attention [1]. Microwave dielectric ceramics can not only be used as insulating substrates material in microwave circuits, also as the key basic material to fabricate dielectric resonators, dielectric filters, dielectric oscillators, phase shifters, microwave capacitors, etc., for microwave communication technology [2]. Therefore, microwave components play an increasingly important role in miniaturization, integration, and cost reduction of modern communication tools [3]. The dielectric materials with high dielectric constant, high Qf value, near-zero temperature coefficient of resonance frequency, and low sintering temperature are strong candidates for 5G technology [4].

The $\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3$ (CLT) ceramic, with typical perovskite structure, is characterized by a high dielectric constant ($\epsilon = 120$) and a high quality factor ($Qf = 10,700$ GHz), but a very high positive resonant frequency temperature coefficient ($\tau_f = 304 \times 10^{-6}/^\circ\text{C}$) [5]. The $\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (NMT) ceramic also has a perovskite structure with Qf value of 36,900~151,000 GHz, the ϵ value is only 25~26, and the τ_f is a large negative value ($-72 \times 10^{-6} \sim -47 \times 10^{-6}/^\circ\text{C}$) [6,7]. The microwave dielectric ceramics with moderate ϵ , high Qf , and τ_f of close to zero can be obtained, by combining $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ or CLT with NMT ceramics [8,9]. However, preparing the CLT-NMT dielectric ceramics by conventional sintering requires excessively high sintering temperature and long sintering time (1650 $^\circ\text{C}$, 3 h; according to our previous work). A small amount of CuO, ZnO and other sintering aids can be added to reduce the sintering temperature [10,11], but it is difficult to avoid the introduction of the second phase and reduction of the microwave dielectric properties.

As an efficient sintering method for materials, microwave sintering can effectively reduce the sintering temperature, increase the sintering rate, and promote the grain re-

finement of ceramics, thus improving the microwave dielectric properties [12,13]. Up to now, there have been no reports on the preparation of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics by microwave sintering. In this work, the $(1-x)\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3-x\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [$(1-x)\text{CLT}-x\text{NMT}$, $x = 0.35\sim 0.60$] ceramics were prepared by microwave sintering and an in-depth study was conducted of the effects of sintering process and component ratio on its phase composition, microstructure, and microwave dielectric properties.

2. Materials and Methods

The $(1-x)\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3-x\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [$(1-x)\text{CLT}-x\text{NMT}$, $x = 0.35\sim 0.60$] ceramics were prepared by the solid-state reaction method. The ingredients were proportioned according to the stoichiometric ratio. High-purity CaCO_3 (99.8%, Langfang Pengcai Fine Chemical, Langfang, China), La_2O_3 (99.9%, Jiangxi Golden Century Advanced Materials Co., Ltd., Nanchang, China), Nd_2O_3 (99.9%, Jiangxi Golden Century Advanced Materials Co., Ltd., Nanchang, China), MgO (99.99%, Jiangxi Golden Century Advanced Materials Co., Ltd., Nanchang, China), and TiO_2 (99.5%, Shanghai Jianglu Titanium Dioxide Chemical, Shanghai, China) powders were mixed by ball mill for 8 h and then dried for 24 h, ground, sieved (200 mesh), and calcined (CLT at 1200°C for 3 h, NMT at 1400°C for 3 h, respectively). Then, the calcined CLT and NMT powders were mixed by ball mill for 8 h, dried for 24 h, and sieved (200 mesh). After added 10 wt % of polyvinyl alcohol solution (PVA, 10%) as a binder, the mixed powders were pressed into columns with a diameter of 13 mm and a thickness of 2~6 mm and then these specimens were heated at 600°C for 1 h to remove the PVA. Finally, these specimens were sintered in air in a microwave sintering furnace (Changsha Longtai Technology Co., Ltd., Changsha, China) ($1475\sim 1575^\circ\text{C}$, 30 min).

The density was measured by the Archimedes method. After crushed and ground, the phase analysis of $(1-x)\text{CLT}-x\text{NMT}$ samples was conducted by X-ray diffraction (XRD, Bruker, Bremen, Germany). After the samples were polished and cleaned with ultrasonic cleaner, etched at 50°C lower than sintering temperature for 30 min, their microstructures were observed by a scanning electron microscope (SEM, FEI, Hillsboro, OR, USA).

To measure the dielectric properties, polished $(1-x)\text{CLT}-x\text{NMT}$ ceramic cylindric specimen was put in a metal cavity of vector network analyzer (N5230A, Agilent Technologies, Loveland, CO, USA), in which high-frequency electromagnetic field can keep oscillating without radiation loss. The dielectric constant (ϵ) and quality factor (Q) were measured at 25°C . The temperature coefficient of resonant frequency (τ_f) was calculated by using the Equation (1):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequency at T_1 (25°C) and T_2 (85°C), respectively.

3. Results and Discussion

3.1. Sintering Characteristics

The influence of sintering temperature on the density (ρ) of $(1-x)\text{CLT}-x\text{NMT}$ ceramics is shown in Figure 1. With the increase of sintering temperature (T), the ρ presents the tendency of increasing first. However, with the further increase of T , the ρ tends to decrease. It may be attributed to oversintering.

The relationship between the ρ and relative density (ρ_r) of the $(1-x)\text{CLT}-x\text{NMT}$ ceramic with x is shown in Figure 2. It can be seen intuitively that the ρ increases with the increase of x , up to 5.457 ($x = 0.60$), mainly because the density of NMT ceramic (6.16 g/cm^3) is higher than that of CLT ceramic (4.51 g/cm^3). The ρ_r is all higher 95.5% with slightly floating and reaches 96.9% when $x = 0.50$.

Figure 1. Bulk density of the (1-x)CLT-xNMT ceramics.

Figure 2. The curves of bulk density and relative density with the composition of (1-x)CLT-xNMT ceramics.

3.2. Phase and Microstructure

The XRD patterns of the (1-x)CLT-xNMT ceramics are illustrated in Figure 3. The diffraction peak positions are almost completely overlapped in the composition range of $x = 0.35\sim 0.60$, indicating a perovskite structure without second phase. It should be pointed out that superlattice diffraction peaks were observed when $x = 0.40$ and 0.45 . The enlarged part of $32.1\sim 33.3^\circ$, as shown in the upper right corner of Figure 3, indicates that the main diffraction peaks of (1-x)CLT-xNMT ceramics shift toward low angle with the increase of x. It suggests the increasing lattice constant of the identified perovskite structure.

Figure 3. XRD patterns of the (1-x)CLT-xNMT ceramics.

The lattice constant (a , b , c) and unit cell volume (V_u) of $(1-x)\text{CLT}-x\text{NMT}$ ceramics are shown in Figure 4. Both lattice constant and unit cell volume gradually increase with the increasing x , which is in accordance with the XRD analysis. This trend depends on two factors: the decreasing vacancy concentration in A -site, the increasing Mg^{2+} content ($r(\text{Mg}^{2+}) > r(\text{Ti}^{4+})$, $r(\text{Mg}^{2+}) = 0.072$ nm, $r(\text{Ti}^{4+}) = 0.061$ nm when CN = 6) in B -site [14], with the increase of NMT content in $(1-x)\text{CLT}-x\text{NMT}$ ceramics.

Figure 4. Lattice constant and unit cell volume of the $(1-x)\text{CLT} - x\text{NMT}$ ceramics.

SEM images of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics (1550 °C, 30 min) are presented in Figure 5. When $x \leq 0.55$, the grain size (10~30 μm) is relatively uniform and change slightly with the increase of NMT content. When $x = 0.60$, the grain size (20~50 μm) is significantly larger than that of the rest composition. When $x < 0.60$, strip-shaped grains can be observed, which is similar to the $\text{CaTiO}_3\text{-La}(\text{Mg}_{0.5}\text{Ti}_{0.5})$ ceramics [15].

Figure 5. SEM images of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics (1550 °C, 30 min): (a) $x = 0.35$, (b) $x = 0.40$, (c) $x = 0.45$, (d) $x = 0.50$, (e) $x = 0.55$, (f) $x = 0.60$.

3.3. Microwave Dielectric Properties

The relationship between dielectric constant (ϵ) and composition of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics is illustrated in Figure 6. With the increase of x , the ϵ gradually decreases from 51.3 to 36.4 because the ϵ of NMT (~ 24) is much lower than that of CLT (~ 120). To evaluate the influence of porosity (p) on the ϵ , the theoretical dielectric constant (ϵ_{th}) of $(1-x)\text{CLT}-x\text{NMT}$ ceramics can be calculated according to the following equation [16,17]:

$$\epsilon_{th} = \epsilon / \left(1 - \frac{3p(\epsilon - 1)}{2\epsilon + 1}\right) \quad (2)$$

where ϵ_{th} is the dielectric constant of a theoretically fully dense ceramic, ϵ is the measured dielectric constant, p is the porosity ($p = 100\% - \rho_r$). Furthermore, Equation (2) can be simplified as follows due to $\epsilon \gg 1$:

$$\epsilon_{th} = \frac{\epsilon}{1 - 1.5p} \quad (3)$$

Figure 6. ϵ and ϵ_{th} of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics.

As shown in Figure 6, the ϵ_{th} of $(1-x)\text{CLT}-x\text{NMT}$ ceramics decreases from 54.2 to 38.3 with the increase of x . It indicates an improvement space of 4.9~6.4%.

The Qf value of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics is presented in Figure 7. It ascends from 13,852 GHz ($x = 0.35$) to 17,148 GHz ($x = 0.40$) and then drops to 8482 GHz ($x = 0.45$) and finally climbs to 32,637 GHz ($x = 0.60$). Generally, the appearance of superlattice diffraction peaks is related to the 1:1 ordering of Mg^{2+} and Ti^{4+} [15], which often affects the dielectric loss and then Qf . The dielectric loss decreases with increasing of ions' degree of order, but increases with attenuation of ions' phonon mode. As x increases to 0.40, the ions' degree of order constantly deepens and the phonon mode attenuates slightly, which results in an increase of Qf . When x climbs to 0.45, the ions' degree of order continues to deepen, but the phonon mode attenuates intensively, which leads to a decrease in Qf . Later, the further increase of x transforms the $(1-x)\text{CLT}-x\text{NMT}$ ceramics from a CLT-based ordered solid solution to an NMT-based ordered solid solution, decreasing dielectric loss, and increasing the Qf value to 32,637 GHz ($x = 0.60$).

Figure 7. The Qf value of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics.

Similarly, the effect of porosity (p) on the Qf value (with $10^3\sim 10^4$ GHz order of magnitude) can be evaluated by the following equation [18]:

$$Q = Q_0(1 - 1.5p) \quad (4)$$

where Q_0 is the intrinsic quality factor, and p is the porosity. The results suggest that an improvement space of 503~1741 GHz.

The temperature coefficient of resonance frequency (τ_f) and tolerance factor (t) of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics are shown in Figure 8. The relationship between the τ_f and temperature coefficient of dielectric constant (τ_ϵ) and linear expansion coefficient (α_L) can be identified as follows [19,20]:

$$\tau_f = -\frac{1}{2}\tau_\epsilon - \alpha_L \quad (5)$$

where the α_L of ceramics is $6\sim 10 \times 10^{-6}/^\circ\text{C}$ [21]. Therefore, the value of the τ_f depends on the τ_ϵ .

Figure 8. τ_f and t of the $(1-x)\text{CLT}-x\text{NMT}$ ceramics.

In 1926, Goldschmidt [22] initially proposed the tolerance factor (t) to evaluate the stability of crystal structure. As to perovskite structure (ABO_3), the t can be calculated according to the following equation [23]:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (6)$$

where R_A , R_B and R_O are the radius of A -site ions, B -site ions and O^{2-} , respectively. The effective ionic radius from Shannon [14] were used to calculate the t of $(1-x)\text{CLT}-x\text{NMT}$ ceramics.

x NMT ceramics. Generally, the t of the perovskite structure should be in the range of 0.77~1.1 and the closer to 1 t is, the stabler the perovskite structure is.

Colla et al. [21] studied the relationship between the tilt of BO_6 octahedron in ABO_3 -type perovskite lattice and the temperature coefficient of dielectric constant (τ_ϵ). The results show that the τ_ϵ is mainly affected by the tilt of BO_6 octahedron. The increasing tilt of BO_6 octahedron will result in the change of the τ_ϵ to the positive direction. The tilt degree of BO_6 octahedron can be described by the t : greater difference between the t value and 1 means greater tilt degree [23]. The τ_ϵ and the t have the following regularity: when $t < 0.965$, the decrease of t will lead to the change of τ_ϵ to the positive direction. For the $(1-x)\text{CLT}-x\text{NMT}$ ceramics, the decrease of t value will lead to the increasing tilt degree of the BO_6 octahedron. Thus the τ_ϵ will increase and the τ_f will decrease to the negative direction, as shown in Figure 8.

Our previous work showed that the conventional sintering procedure of $(1-x)\text{CLT}-x\text{NMT}$ ceramics was sintering at 1650 °C for 3 h. In the present work, microwave sintering processes effectively promoted the densification of $(1-x)\text{CLT}-x\text{NMT}$ ceramics with lower sintering temperature (1475 °C) and shorter sintering time (30 min). Chen et al. [9] prepared $0.40\text{Nd}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.60\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ (with 1 wt % B_2O_3 as sintering additive) ceramics via conventional sintering (1375 °C, 3 h) with excellent microwave dielectric properties: $\epsilon = 49$, $Qf = 13,000$ GHz, $\tau_f = 1 \times 10^{-6}/^\circ\text{C}$. As compared to Chen's work, microwave sintered $0.65\text{CLT}-0.35\text{NMT}$ ceramics (without sintering additive, 1550 °C, 30 min) also possesses similar microwave dielectric properties: $\epsilon = 51.3$, $Qf = 13,852$ GHz, $\tau_f = -1.9 \times 10^{-6}/^\circ\text{C}$.

4. Conclusions

The $(1-x)\text{Ca}_{0.61}\text{La}_{0.26}\text{TiO}_3-x\text{Nd}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [$x = 0.35\sim 0.60$, $(1-x)\text{CLT}-x\text{NMT}$] ceramics were prepared by microwave sintering. The effects of sintering process and component distribution compare on its phase composition, microstructure, and microwave dielectric properties were investigated. Microwave sintering can effectively reduce the sintering temperature and the sintering time. The $(1-x)\text{CLT}-x\text{NMT}$ ceramics have formed a perovskite structure. As x increases, the ϵ shows a downward trend, the Qf first drops to 8482 GHz and then rises to 32,637 GHz, and the τ_f keeps decreasing. When $x = 0.35$, the comprehensive microwave dielectric performance is: $\epsilon = 51.3$, $Qf = 13,852$ GHz, $\tau_f = -1.9 \times 10^{-6}/^\circ\text{C}$ (1550 °C, 30 min). The $(1-x)\text{CLT}-x\text{NMT}$ ceramics can be applied to the field of mobile communications.

Author Contributions: Conceptualization, writing—review and editing, funding acquisition, and supervision: B.L.; methodology, investigation, data curation, and writing—original draft preparation: S.Y., J.L., and C.F.; visualization, and validation: C.L.; project administration, and resources: Y.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (51664043), the Natural Science Foundation of Jiangxi Province (20192BAB206007), and the Key Laboratory for Microstructural Control of Metallic Materials of Jiangxi Province (Nanchang Hangkong University) Open Fund (EJ201901455).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Zhou, D.; Pang, L.; Wang, D.; Reaney, I.M. BiVO₄ based high k microwave dielectric materials: A review. *J. Mater. Chem. C* **2018**, *6*, 9290–9313. [\[CrossRef\]](#)
2. Wang, D.; Zhang, S.; Zhou, D.; Song, K.; Feteira, A.; Vardaxoglou, Y.; Whittow, W.; Cadman, D.; Reaney, I.M. Temperature stable cold sintered (Bi_{0.95}Li_{0.05})(V_{0.9}Mo_{0.1})O₄-Na₂Mo₂O₇ microwave dielectric composites. *Materials* **2019**, *12*, 1370. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Wersing, W. Microwave ceramics for resonators and filters. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 715–731. [\[CrossRef\]](#)
4. Wang, S.; Luo, W.J.; Li, L.X.; Du, M.K.; Qiao, J.L. Improved tri-layer microwave dielectric ceramic for 5G applications. *J. Eur. Ceram. Soc.* **2021**, *41*, 418. [\[CrossRef\]](#)
5. Liang, B.L.; Zheng, X.H.; Ni, W.Q.; Tang, D.P. Ca_{1-3x}Ln_{2x}TiO₃ ($x = 0.13, 0.2$; Ln=La, Nd, Sm): High ϵ microwave dielectric ceramics. *Rare Met. Mater. Eng.* **2007**, *36*, 418–421. (In Chinese)
6. Seabra, M.P.; Salak, A.N.; Avdeev, M.; Ferreira, V.M. Structure and dielectric characterization of the La(Mg_{1/2}Ti_{1/2})O₃-Nd(Mg_{1/2}Ti_{1/2})O₃ system. *J. Phys. Condens. Matter* **2003**, *15*, 4229–4238. [\[CrossRef\]](#)
7. Kim, J.B.; Yoon, K.H.; Cho, Y.S. Compositional dependence of microwave dielectric properties in (1-x)(Na_{1/2}Nd_{1/2})TiO₃-xNd(Mg_{1/2}Ti_{1/2})O₃ ceramics. *J. Am. Ceram. Soc.* **2003**, *86*, 1159–1161. [\[CrossRef\]](#)
8. Lin, S.H.; Chen, Y.B. Structure and characterization of B₂O₃ modified yNd(Mg_{1/2}Ti_{1/2})O₃-(1-y)Ca_{0.8}Sr_{0.2}TiO₃ ceramics with a near-zero temperature coefficient at microwave frequency. *Ceram. Int.* **2017**, *43*, 2368–2371. [\[CrossRef\]](#)
9. Chen, Y.B. Structure and dielectric characterization of xNd(Mg_{1/2}Ti_{1/2})O₃-(1-x)Ca_{0.6}La_{0.8/3}TiO₃ in the microwave frequency range. *J. Alloys Compd.* **2011**, *509*, 6285–6288. [\[CrossRef\]](#)
10. Chen, Y.B. Structural and dielectric properties of La(Mg_{1/2}Ti_{1/2})O₃-Ca_{0.6}La_{0.8/3}TiO₃-doped CuO. *J. Alloys Compd.* **2009**, *480*, 820–823. [\[CrossRef\]](#)
11. Chen, Y.B. New dielectric material system of La(Mg_{1/2}Ti_{1/2})O₃-Ca_{0.6}La_{0.8/3}TiO₃ for microwave applications. *J. Alloys Compd.* **2009**, *480*, 265–269. [\[CrossRef\]](#)
12. Tian, L.; Nan, J.; Wang, H.; Shen, C. Effect of microwave sintering on the properties of 0.95(Ca_{0.88}Sr_{0.12})TiO₃-0.05(Bi_{0.5}Na_{0.5})TiO₃ ceramics. *Materials* **2019**, *12*, 803. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Benavente, R.; Salvador, M.D.; Centeno, A.; Alonso, B.; Zurutuza, A.; Borrell, A. study of microwave heating effect in the behaviour of graphene as second phase in ceramic composites. *Materials* **2020**, *13*, 1119. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **1976**, *32*, 751–767. [\[CrossRef\]](#)
15. Kipkoech, E.R.; Azough, F.; Freer, R. Microstructural control of microwave dielectric properties in CaTiO₃-La(Mg_{1/2}Ti_{1/2})O₃ ceramics. *J. Appl. Physiol.* **2005**, *97*, 1–11. [\[CrossRef\]](#)
16. Luo, W.; Guo, J.; Randall, C.; Lanagan, M. Effect of porosity and microstructure on the microwave dielectric properties of rutile. *Mater. Lett.* **2017**, *200*, 101–104. [\[CrossRef\]](#)
17. Penn, S.J.; Alford, N.M.; Templeton, A.; Wang, X.; Xu, M.; Reece, M.; Schrapel, K. Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. *J. Am. Ceram. Soc.* **1997**, *80*, 1885–1888. [\[CrossRef\]](#)
18. Kim, E.S.; Park, H.S.; Yoon, K.H. Porosity dependence of microwave dielectric properties of complex perovskite (Pb_{0.5}Ca_{0.5})(Fe_{0.5}Ta_{0.5})O₃ ceramics. *Mater. Chem. Phys.* **2003**, *79*, 213–217. [\[CrossRef\]](#)
19. Kajfez, D. Temperature characterization of dielectric–resonator materials. *J. Eur. Ceram. Soc.* **2001**, *21*, 2663–2667. [\[CrossRef\]](#)
20. Xiong, Z.; Tang, B.; Luo, F.C.; Yang, H.Y.; Zhang, X.; Yang, C.T.; Fang, Z.X.; Zhang, S.R. Characterization of structure, chemical bond and microwave dielectric properties in Ca_{0.61}Nd_{0.26}TiO₃ ceramic substituted by chromium for titanium. *J. Alloys Compd.* **2020**, *835*, 155249. [\[CrossRef\]](#)
21. Colla, E.L.; Reaney, I.M.; Setter, N. Effect of structural changes in complex perovskites on the temperature coefficient of the relative permittivity. *J. Appl. Physiol.* **1993**, *74*, 3414–3425. [\[CrossRef\]](#)
22. Goldschmidt, V.M. The laws of crystal chemistry. *Naturwissenschaften* **1926**, *14*, 477–485.
23. Reaney, I.M.; Colla, E.L.; Setter, N. Dielectric and structural characteristics of Ba– and Sr–based complex perovskites as a function of tolerance factor. *Jpn. J. Appl. Phys.* **1994**, *33*, 3984–3990. [\[CrossRef\]](#)